

Stratospheric ozone profiles from Mauna Kea, Hawai'i (19.8°N, 155.5°W) using infrared heterodyne spectroscopy, 1988–2003

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[1] We present stratospheric ozone abundance profiles retrieved from absorption spectroscopy of the atmosphere backlit by thermal continuum emission of the Moon. Infrared heterodyne spectra at 9.6 μm at a resolving power of $\lambda/\Delta\lambda \geq 10^6$ have been acquired on many occasions between 1988 and 2003 from the NASA Infrared Telescope Facility on Mauna Kea, Hawai'i. IR heterodyne spectroscopy provides a passive probe of terrestrial ozone distribution in the 25–50 km region of the stratosphere with the potential to retrieve altitude-resolved profiles of temperature and abundance. Retrieved ozone profiles are compared with those obtained nearby using active and in situ means (lidar, ozonesonde) with good agreement (≤ 0.1 ppmv) in the lower stratosphere and with differences ranging from 0 to 1 ppmv in the upper stratosphere.

INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325).

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1. Introduction

[2] Ozone is an important stratospheric constituent because of its role in shielding the biosphere from solar ultraviolet radiation and its participation in maintaining the atmosphere's radiative balance. Ozone abundance and distribution are variable and influenced by solar activity, season, homogeneous and heterogeneous chemistry, circulation and mixing, and tropospheric activity. Long-term monitoring of ozone is important to understanding and quantifying natural vs. anthropogenic causes of variability.

[3] Active and passive remote techniques (e.g., lidar, microwave, Umkehr) and in situ probes (ozonesonde) are employed routinely around the world in order to measure the vertical profile of ozone in the local stratosphere, and ozone column abundance is acquired passively through the Dobson technique [e.g., *McPeters et al.*, 1999]. A passive means of probing the height distribution of ozone is infrared heterodyne spectroscopy.

[4] The very high spectral resolution of infrared heterodyne spectroscopy ($\lambda/\Delta\lambda \sim 10^6$ – 10^7) results in fully resolved ro-vibrational molecular lineshapes, providing the basis for partial discrimination between molecular abundance and temperature [e.g., *Fast et al.*, 2002; *Livengood et al.*, 1993; *Kostiuk and Mumma*, 1983; *Kostiuk et al.*, 1997], within the limits imposed by noise. Infrared heterodyne spectroscopy has been applied to the study of planetary atmospheres [cf. *Kostiuk*, 1994] as well as to the study of height profiles of terrestrial stratospheric constituents such as ozone [e.g., *Frerking and Muehler*, 1977; *Abbas et al.*, 1979; *Fukunishi et al.*, 1990; *McElroy et al.*, 1990; *Sonnabend et al.*, 2002], and methane [*Koide et al.*, 1995]. The terrestrial ozone spectra employed here were acquired as part of campaigns between 1988 and 2003 on Mauna Kea, Hawai'i to measure ozone abundance on Mars. Spectra of telluric ozone absorption in contrast against thermal emission by the Moon were acquired in order to characterize and remove the terrestrial component from the Mars spectra [*Espenak et al.*, 1991]. We present ozone height profiles retrieved from these spectra, the details of the retrievals, and comparison to contemporaneous measurements made elsewhere on the Big Island of Hawai'i. Dobson total ozone column densities [*Komhyr et al.*, 1997] and lidar ozone profiles [*McDermid et al.*, 1995] utilized in this work were measured at the Mauna Loa Observatory (MLO), and ozonesonde measurements were made from Hilo, HI [*Johnson et al.*, 2002].

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2. Data Acquisition and Analysis

[5] The data described in this work were acquired with the NASA/Goddard Infrared Heterodyne Spectrometer (IRHS) and the Heterodyne Instrument for Planetary Wind and Composition (HIPWAC) at the NASA Infrared Telescope Facility (IRTF) on Mauna Kea, Hawai'i (19.8°N

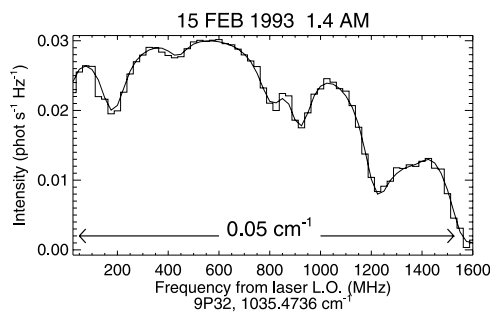


Figure 1. Example heterodyne spectrum against the Moon (histogram) using a 9 μm P32 CO_2 laser local oscillator (1035.4736 cm^{-1}). Individual ozone absorption features are resolved and matched by a radiative transfer model (solid line). The displayed spectrum is as double sideband, as measured; i.e., spectrum is the sum of upper and lower sidebands.

155.5°W). A detailed discussion of the infrared heterodyne technique utilized here is given by *Kostiuk* [1994] and by *Kostiuk and Mumma* [1983]. Infrared light from a remote or laboratory source is mixed with light from an infrared CO_2 laser local oscillator and focused onto a HgCdTe photomixer. This results in a beat frequency spectrum that is in the radio regime, preserving the frequency and intensity information of the infrared spectrum. Analysis using RF techniques yields the spectrum within the bandwidth of the photomixer, $\pm 1600\text{ MHz}$ from the laser frequency. In this work, a $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ gas laser was tuned to either the 9 μm P32 (1035.4736 cm^{-1}) or the 9 μm P36 (1031.4774 cm^{-1}) transition. The spectral regions around these transitions contained strong ozone lines as well as spectral structure that allowed corresponding Mars ozone lines to be Doppler shifted into regions of higher terrestrial transmittance. A local blackbody source provided the system intensity calibration, which was compared with direct lunar measurement. The accuracy in the measured intensities is $\leq 3\text{K}$. The RF filter bank used to analyze the signal contains 64 filters that are 25 MHz (0.00083 cm^{-1}) in width, providing 3200 MHz of frequency range folded into a 1600 MHz double-sideband spectrum.

[6] Absorption spectra of the Earth's atmosphere against the Moon were taken. Over the spectral range of these measurements, the Moon's thermal continuum is essentially flat. Features in the spectrum represent the variation of the Earth's atmospheric transmittance due to absorption by ozone and by carbon dioxide (which is weak in this interval). Spectra were acquired at multiple values of air mass. Individual integrations lasting 3–6 minutes each were averaged into bins of 0.1 air mass for comparison to model spectra (Figures 1 and 3).

[7] The transmittance of the terrestrial atmosphere is modeled using the line-by-line radiative transfer package GENLN2 [Edwards, 1992]. The radiance of the atmosphere also is modeled and, although minor, is taken into account in this analysis. A standard atmospheric model is modified to produce radiative transfer model spectra consistent with the data. The starting-point temperature and molecular mole fraction profiles are from the AFGL tropical (15°N) atmospheric model [Anderson et al., 1986] consistent with the $\sim 20^\circ\text{N}$ latitude of Mauna Kea. The profiles and the regions

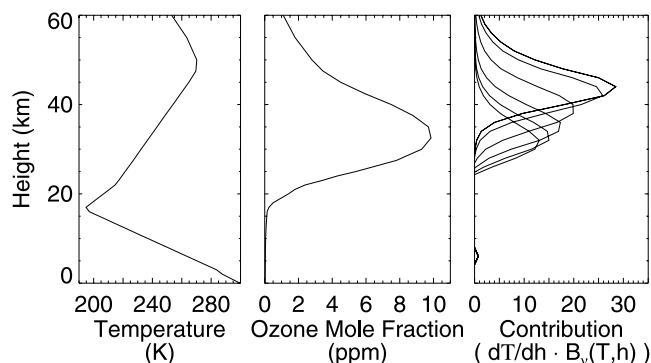


Figure 2. AFGL tropical (15°N) thermal and ozone model fraction profiles [Anderson et al., 1986]. These are used as a starting point for radiative transfer modeling of the heterodyne spectra. Contribution functions are shown for the center (uppermost profile) and wings (lower profiles, 200 MHz increments) of one of our target ozone absorption features.

of greatest contribution to our spectra are shown in Figure 2. The infrared heterodyne spectra are most sensitive to the 25–50 km region with an altitude resolution of $\sim 8\text{ km}$. The stratospheric portions of the ozone mole fraction profile and the temperature profile are modified by scale factors and corresponding GENLN2 radiative transfer models of the emergent spectrum are generated, resulting in a library of candidate model spectra corresponding to a grid of model parameters. A similar library of model spectra is generated for each 0.1 air mass bin required by the data. When a grid of models is compared to one of our heterodyne spectra, a grid of RMS values results. The Fisher F-statistic (also known as the ratio-of-variances method) is used to determine the region around the best-fit stratospheric ozone mole fraction and temperature profile scale factors (Figure 3) that meets a 1-sigma confidence criterion. The best-fit parameters from multiple spectra were combined statistically according to the estimated variance of each retrieved parameter, resulting in our profiles and error bars (Figures 3 and 4).

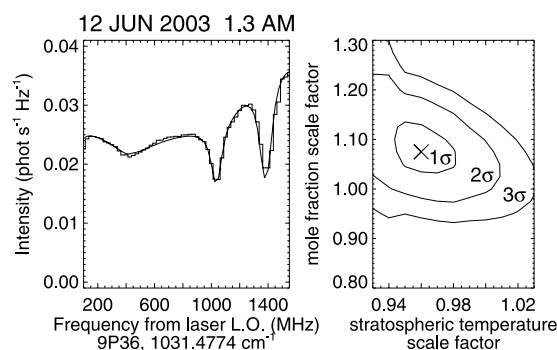


Figure 3. The contour plot indicates how well radiative transfer models using different scalings of the thermal and ozone mole fraction profiles fit the spectrum at left. The “X” marks the best-fit parameters, which produce the model spectrum shown at left (solid line) compared to the heterodyne spectrum (histogram) that used a 9 μm P36 CO_2 laser local oscillator (1031.4774 cm^{-1}).

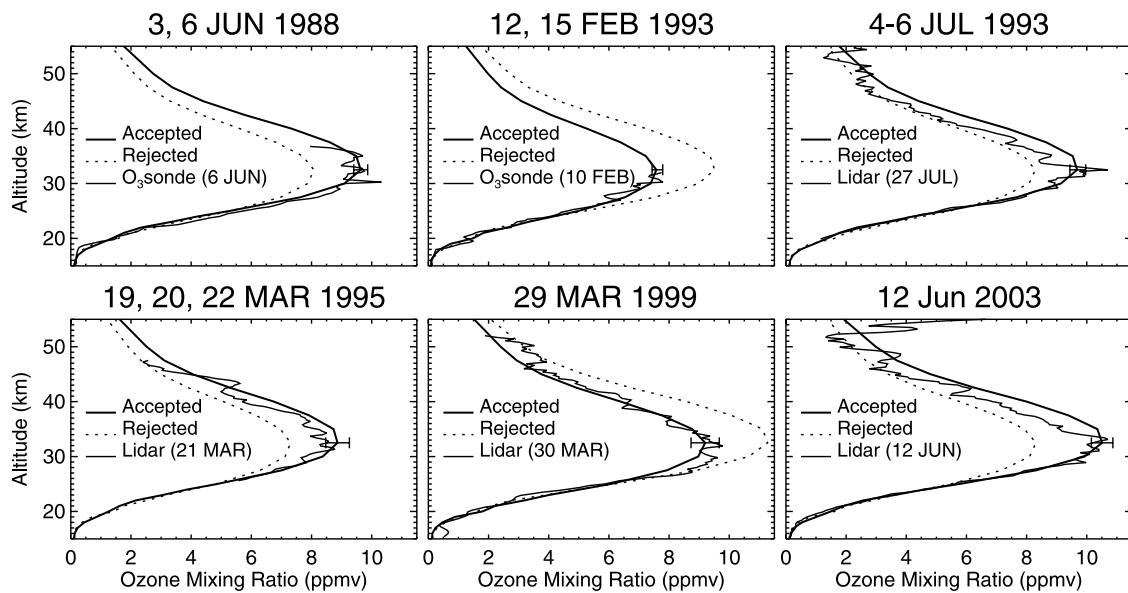


Figure 4. Model profiles and 1σ uncertainties retrieved from heterodyne spectra compared to available nearby lidar [McDermid *et al.*, 1995] or ozonesonde [Johnson *et al.*, 2002] profiles. The bold profiles indicate those chosen according to column density (see Table 1). The dotted profiles are model profiles that fit the spectra adequately, yet were rejected because the total ozone column densities were not consistent with those from Dobson spectrophotometer observations. The model profiles result from applying scale factors to a standard tropical ozone profile in the process of fitting radiative transfer model spectra to heterodyne spectra. The error bar at each ozone peak illustrates the range of statistically acceptable (1σ) scaled profiles. Because a scale factor is applied to the entire mixing ratio profile, the error bar range is scaled accordingly as a function of mixing ratio, and thus decreases away from the peak.

[8] Although the altitude of the ozone peak is not highly variable at this latitude, the range of variation was explored in order to introduce reasonable profiles into the radiative transfer modeling. We fit the stratospheric part of the AFGL ozone profile to MLO lidar ozone profiles from many years by applying a scaling factor and by shifting the stratospheric ozone in altitude. In many cases, the AFGL profile had to be shifted down 1 km in altitude in order to fit the lidar data. Therefore, in addition to the GENLN2 models described earlier, model spectra were generated with the stratospheric portion of the ozone profile shifted down 1 km in altitude. Both sets of model spectra were compared to the heterodyne data and the best fits of the two altitude cases to a heterodyne spectrum were usually statistically indistinguishable from each other. There was no evident correlation between the two altitude cases and the precision of the fit. However, the MLO Dobson total ozone column density measurements can provide an additional constraint which points to one of the two models. We found that this method produced

model ozone profiles consistent with those measured through active and in situ means (lidar, ozonesonde).

3. Results and Comparison to Other Methods

[9] Column densities retrieved from the best-fit models are presented in Table 1. The Dobson measurements [Komhyr *et al.*, 1997] are compared to radiative transfer fits obtained using a scaled AFGL profile, as well as that same profile shifted down 1 km before scaling. In choosing between these two cases, we prefer the case in which the Dobson measurements agree with our own retrieval and use the selected abundance profile and temperature profile scale parameters. This is checked in Figure 4, where the retrieved model profiles themselves are compared to nearby ozonesonde and lidar profiles. The bold profiles are those chosen based on their consistency with Dobson column density measurements as just described. The dotted profiles were rejected because of inconsistency with the column densities retrieved from Dobson spectro-

Table 1. Total Ozone Column Density Retrievals

Date (UT)	IRHS retrieval (D.U.) Using Scaled AFGL Profile		MLO Retrieval From Dobson Spectrophotometer Instrument No. 76 (D.U.)
	Not Shifted in Altitude	Shifted -1 km in Altitude	
1988 June 3, 6	260 ± 9^a	250 ± 10	$263 \pm 1\%$ (6/3/88), $269 \pm 5\%$ (6/6/88)
1993 February 12, 15	254 ± 10	236 ± 7^a	$240 \pm 2.4\%$ (2/12, 14/93)
1993 July 4–6	265 ± 8^a	257 ± 9	$267 \pm 1\%$ (7/6/93)
1995 March 19, 20, 22	235 ± 13^a	229 ± 10	$261 \pm 1\%$ (3/6/95), $238 \pm 1\%$ (3/28/95)
1999 March 29	299 ± 15	287 ± 16^a	$277 \pm 1\%$
2003 June 12	280 ± 14^a	227 ± 10	$279 \pm 1\%$

^aBest fit according to Dobson measurements.

photometer measurements. The model profiles chosen using this column density criterion are consistent with available ozonesonde and lidar measurements.

[10] For the three summer measurements, the unshifted ozone profile provided satisfactory fits to the heterodyne spectra and column densities consistent with Dobson measurements, with high ozone abundances as expected in summer. The winter measurements show less similarity in their ozone profile retrievals. Sources of long term and short term variability (e.g., transport, solar activity, chemistry, tropospheric activity) need to be further investigated. The 2/93 and 3/99 measurements required that the model ozone profile be shifted down 1 km in altitude and scaled in order to both fit the spectra and agree with Dobson column densities. The 3/99 measurement made during the strong La Niña of '98–'00, however, had a much higher stratospheric ozone mole fraction and total column density. The 3/95 measurement made near solar minimum did not require an altitude shift in the mole fraction profile like the other winter measurements and was similar in column density to that of 2/93, but with a higher mole fraction due to the slightly higher altitude distribution. Day to day variations due to transport phenomena can also be responsible for the observed profile changes.

[11] The altitude shift we employ is slight and is consistent with adjustments to bring the standard AFGL profile into agreement with individual lidar scans, and may represent variability in particular altitude regions rather than a vertical shift of the ozone peak. For instance, *Leblanc and McDermid* [2000] examined lidar ozone profiles over a 6-year period at Mauna Loa and did not note any significant altitude shift of the ozone peak, but they did note some seasonal variation in the 30 km region and high variability in the 18 km region in addition to the seasonal variation of the overall ozone profile. The behavior in the 18 km region was attributed to high tropopause altitude and variability, and may be responsible for our variety of winter model ozone altitude distributions more so than solar activity.

4. Conclusions

[12] We have presented ozone profile retrievals from infrared heterodyne absorption spectra taken against the Moon between 1988 and 2003 on Mauna Kea, Hawai'i. Our method scaled the stratospheric part of the AFGL tropical ozone and thermal profiles as input to a radiative transfer model to produce model spectra for comparison with the data. In some cases, ozone profiles that were shifted down 1 km in altitude were required both to produce good fits to the spectra and to provide ozone column densities in agreement with measured Dobson column densities. The resulting profiles with column densities ranging from 235–287 D.U. agree well with other techniques that probe the altitude distribution of stratospheric temperature and pressure. Total uncertainties include radiance calibrations and precision of fits (Table 1). The scaling of a standard profile to obtain total ozone column densities from heterodyne spectra has been done elsewhere [e.g., *Mouanda et al.*, 1996]. We have found that shifting a standard ozone profile in altitude slightly can yield an equally acceptable fit to a heterodyne spectrum, yet this results in different column abundances. The total ozone column densities as measured by other means, e.g., Dobson

spectrophotometry, can be used to obtain unique results from our data.

[13] Infrared heterodyne spectroscopy has the potential to provide important new information regarding the structure of the stratosphere. In the present work, using data not explicitly targeted for this topic, we have demonstrated the ability to obtain altitude profiles of temperature and ozone concentration consistent with results of active lidar measurements and in situ ozonesonde probes, using only a modest additional constraint on the total ozone column. Ground based IR heterodyne spectroscopy provides ≤ 8 km altitude resolution using a passive technique with relatively modest power requirements and durable equipment and is not limited to ozone. Other species of interest, such as water and ClO [e.g., *Mumma et al.*, 1983], are accessible to direct measurement contemporaneous with ozone measurements, enabling regular monitoring of ozone chemistry using repeatable passive observations.

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